

Things of science

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CORROSION

Unit No. 335

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CORROSION

This unit of THINGS of science contains four types of nails, three different metal wires and a magnesium ribbon.

Rusty nails and tarnished silver are not unusual sights in our daily lives, and we consider them more as nuisances than serious problems.

However, to chemists, metallurgists and engineers, they represent one of the major problems encountered in the use of metals, corrosion.

Almost all metals corrode to some extent, but when corrosion is mentioned, it is usually in reference to iron and its alloys because of the importance and wide usage of this metal and the ease with which it rusts unless protected.

Corrosion is expensive. Each year a large part of the steel produced is used to replace steel weakened and destroyed by corrosion. Since corrosion is an irreversible process, metal that becomes corroded is lost and wasted.

What is corrosion and how can it be controlled? The experiments in this unit will help you understand how corrosion occurs and the methods used for its prevention.

First examine your specimens.

PLAIN STEEL NAILS—Twelve nails;

one inch long; flat head.

GALVANIZED NAILS—Three nails; zinc plated; $1\frac{3}{8}$ inches long; flat head.

NICKEL PLATED NAILS—Three nails; $1\frac{1}{8}$ inches long; brad head; bright silvery color.

COPPER PLATED NAILS—Two nails; one inch long; reddish in color.

MAGNESIUM RIBBON—Flat ribbon; $\frac{1}{8}$ -inch wide; 12 inches long.

ALUMINUM WIRE—Six inches long.

COPPER WIRE—Ten inches long.

LEAD WIRE—Four inches long.

WHAT IS CORROSION?

Most metals are found in nature as ores in combination with one or more other elements. This is because, except for a few such as gold and platinum, metals readily combine with other elements and compounds to form oxides and salts.

Although corrosion may be considered as the chemical destruction of metal, it is actually the return of a metal to its natural state.

For example, iron, abundantly present in the earth's crust, occurs primarily as the reddish ore hematite, which is the iron oxide, Fe_2O_3 , chemically the same as rust. Iron may also corrode by forming the black iron oxide, Fe_3O_4 , found in na-

ture as the ore magnetite. Other metals also corrode by returning to their natural oxide or salt.

Metals to be utilized must be refined, a process which usually involves the application of heat. The more active a metal, the more heat required to purify it; and the more inclined it is to give up this energy, the more easily it will corrode.

What takes place during corrosion? The theory is that an electrochemical reaction, a reaction similar to that which occurs in a battery, goes on during corrosion.

A flow of energy in the form of electricity occurs from one surface of a metal to another through a suitable medium, an electrolyte.

An electrolyte is any liquid containing positive and negative ions, such as a salt, acid or just plain water. Water, ever present around us in atmosphere, soil and sea, is the most common electrolyte. It contains positively charged hydrogen ions (H^+) and negatively charged hydroxyl ions (OH^-).

Certain conditions are necessary for corrosion to occur. There must be an electrolyte through which an electric current can travel, two metal surfaces and a bridge that will allow continuous current flow.

No outside source of electricity is necessary.

The bridge between two different metals may result from direct contact between the metals as in the experiments you will perform or by connecting the metals with a wire (Fig. 1).

Whenever a metal is exposed to an electrolyte, it acquires an electric potential which depends upon the type and purity of the metal, the composition of the electrolyte, and the condition of the metal surface.

A difference in the potential of two metal surfaces causes a flow of electrons to occur. The surface from which the

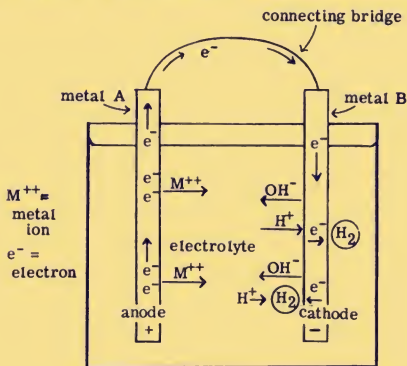


Fig. 1

electrons originate is called the anode or the positive electrode, and the surface receiving the electrons is termed the cathode, the negative electrode.

An electrolytic cell is formed because one metal is more active than the other or one surface of a metal is more active than another part of the same piece of metal, resulting in a potential difference between the two surfaces.

Corrosion cells may result from the presence of two different metals or a mixture of two metals as in an alloy. This is known as galvanic action.

Steel, an alloy, is more inclined to rust than wrought iron which is almost pure iron and thus has less likelihood of galvanic action taking place.

We can predict the amount of activity that will occur within an electric cell by knowing the voltage that is developed between different metals. The list of metals according to their activity is known as the electromotive series.

Below is a list of some of the more common metals in this series arranged in the order of decreasing chemical activity.

potassium
barium
calcium
sodium

magnesium
aluminum
zinc
chromium
iron
nickel
tin
lead
hydrogen
copper
silver
platinum
gold

When any two of the above metals are placed in an electrolyte in contact with each other, the more active of the two, the one losing energy, will more likely be attacked by corrosion. The two metals in contact and the electrolyte form a closed electric circuit. The less active of the two will usually remain uncorroded. The further apart a pair of metals are in the electromotive series, the more rapidly the more active one will corrode. The more active metal becomes the anode and the less active the cathode.

You will note that we have included hydrogen in the list. It acts as a dividing line between the metals. All of the metals listed above hydrogen will liberate it from acids or water while those listed below it

will not.

In corrosion, the metal loses electrons and their atoms become ions which go into solution. This causes the metal, or anode, to lose atoms, and eventually it will completely disappear. This ionization of the metal is the basis of corrosion. You have probably seen holes in rusted structures of iron sheeting. The iron in those parts was dissolved away by ionization.

Experiment 1. The plain steel nail in your unit is made of low carbon steel.

In order for iron to rust, moisture must be present.

Place one of your plain steel nails in a small covered glass jar and set it aside. Look at it from time to time for a week or more. Does it rust? Iron will not rust in dry air.

Experiment 2. Place a one-inch strip of each of the wires, copper, aluminum and lead, and of the magnesium ribbon in separate containers of tap water. Place a nail in another jar of tap water. Allow all the specimens to stand overnight, then examine them. Which ones show the most corrosion? Note the position of each of the metals in the electromotive series.

You will see evidences of reaction in

the magnesium and iron.

Although aluminum is more active than iron, no reaction appears. It reacts quickly when exposed to the atmosphere. However, it forms a highly durable film of aluminum oxide (Al_2O_3) on its surface which prevents further reaction and protects the aluminum beneath from further corrosion.

Lead is low in the activity list and does not readily corrode.

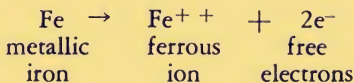
Copper, still lower on the scale is not affected by immersion in water. Copper which is resistant to atmospheric corrosion, in humid areas forms a bright coating of copper oxide (Cu_2O). With continued exposure it turns a dull green, by combining with the sulfur and carbon dioxide in the air to form a complex copper salt. Most of you have seen this evidence of copper corrosion on copper roofs or bronze statues.

Experiment 3. Without moving the jar or disturbing the solution in any way, carefully examine the plain steel nail in the tap water again. Where does the nail show rusting?

In order for corrosion to occur, a closed electric cell must be present with an anode and a cathode. The area in which the rusting is evident is the anode and the clear

area the cathode. Different potentials exist in different parts of a metal alloy causing electricity to flow. In fact, each little tiny point at which corrosion occurs results from a tiny electric cell with its own anode and cathode.

When iron corrodes, the half reaction that takes place at the anode is represented below.



The metallic iron loses two electrons or negative charges and goes into solution as the positively charged ferrous ion. The free electrons create the electric current.

When rust forms, the iron ions combine first with the hydroxyl ions in the water to form ferrous hydroxide which you cannot see. This then oxidizes into hydrated iron oxide ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) which gives iron its familiar reddish color.

Whenever corrosion occurs, hydrogen gas is produced leaving free hydroxyl ions in solution. These ions make the area they occupy slightly alkaline.

The hydrogen ions in the water take up the electrons released by the iron at the anode, and combine to form hydro-

gen gas. In very active reactions, this is evident as bubbles at the cathode.

For iron to rust, oxygen too must be present to oxidize the ferrous hydroxide, initially formed by the combination of the hydroxide ions and ferrous ions, into the iron oxide, Fe_2O_3 .

The rust may be deposited on the surface of the nail, or if shaken will fall to the bottom of the jar.

If the solution is aerated and more oxygen introduced into it, corrosion will be speeded up.

If it remains undisturbed, the potential difference between the two metals or areas of the two metals tends to become decreased and corrosion is slowed or stopped.

Experiment 4. Place another plain steel nail in water and shake it from time to time as rust forms to aerate the solution and expose the surface. Does this nail corrode more rapidly than the undisturbed nail?

Experiment 5. Bend one of your plain steel nails and place in water. Where does corrosion begin in this nail?

Strained areas in metals corrode more readily than unstrained areas.

Heat also speeds up corrosion.

GALVANIC CORROSION

The corrosion that occurs when two unlike metals are placed in an electrolyte in contact with each other is known as galvanic corrosion.

In any two-metal combination the more active metal will be the anode and the less active the cathode.

Experiment 6. Cut a $3\frac{1}{2}$ -inch strip of the magnesium ribbon and wind one end around the plain steel nail just beneath the head and place in tap water (Fig. 2). Be sure the magnesium ribbon and nail are in contact. Examine the next day. You should find the nail unrusted and its surface unchanged.

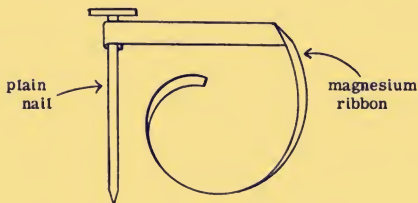


Fig. 2

The magnesium is the anode and the steel the cathode. The magnesium protects the nail from corrosion by corroding itself. This is known as cathodic protection.

Cathodic protection is used to prevent corrosion of iron pipes buried in the ground. Magnesium bars are connected to the iron pipe by means of wires and the magnesium being the more active metal, corrodes away while the iron remains rust free. This is an example of sacrificial corrosion. The magnesium is sacrificed to protect the iron pipe. A similar usage is made of magnesium to protect the steel bottom of some ships and the inside of hot water tanks.

As the magnesium is used up, it is replaced to provide continuous protection.

Experiment 7. After a few days note that a whitish deposit has formed at the point of contact between the nail and the magnesium. The deposit is magnesium oxide, evidence of the galvanic corrosion suffered by the magnesium.

Experiment 8. Cut a 3-inch piece from your aluminum wire and wind it around one end of a plain steel nail.

Immerse in water. Does the aluminum protect the nail?

Although aluminum is higher in the activity series than iron, it will not protect it from corrosion because of the aluminum oxide on its surface.

Experiment 9. Cut a 3-inch piece of copper wire and wind one end around

a plain nail and immerse in water. Observe the next day. What results do you observe? Which metal is the anode and which the cathode?

Did the metals react as would be expected from the electromotive series?

Experiment 10. Wind a 3-inch length of the copper wire in the same way around the galvanized nail. Does this nail corrode also? Does it take longer to show signs of corrosion? Why doesn't the zinc protect the iron against copper?

Why is it unwise to connect a copper pipe directly to an iron pipe in a water system, or use copper rivets to secure steel sheeting even if galvanized?

Experiment 11. Place a plain steel nail into a dilute solution of table salt, sodium chloride, (about $\frac{1}{8}$ teaspoon table salt in a half a cup of water) and another nail in a more concentrated solution of sodium chloride (2 teaspoons salt in a half cup of water).

Do you find any differences in the corrosion rate as compared to the nail in the dilute salt solution?

Is the corrosion more rapid in this solution than in tap water?

Is corrosion more pronounced in the dilute than in the concentrated solution of sodium chloride?

Sodium chloride in concentrations of about 3%, the same as that in seawater, causes the greatest amount of corrosion in iron. As concentrations become less than or greater than 3%, corrosion decreases.

Dilute acids also attack metals such as aluminum, magnesium, tin, iron and lead. These metals go into solution releasing hydrogen gas.

Experiment 12. Examine a rusted object and note the brown color. Note that its surface is porous, and if badly rusted that it is flaky. Unlike aluminum oxide, iron oxide does not form a thin film and protect the surface beneath. Its uneven surface absorbs moisture and traps the air, contributing to further corrosion. Therefore, once iron begins to corrode it continues to do so steadily unless preventive measures are taken. Once started, corrosion will even eat under a protective surface.

Experiment 13. Examine the surface of one of your corroded nails. Note that it is rough and the luster of the metal has completely disappeared. Examine under a magnifying glass. Is the surface smooth or pitted with tiny holes?

Experiment 14. Cut a 2-inch piece from your lead wire and wind one end around the galvanized nail. Then place

in a container of tap water. What happens to the nail? Why?

Experiment 15. Place the rest of the lead in contact with an equal length of copper wire and place in tap water. Do you get any reaction?

Lead and copper in contact with each other are not mutually destructive. Note their relative positions in the electromotive series.

Experiment 16. Corrosion can occur when the oxygen concentration on one area of a metal differs from that on another area because of the impurity of the water or because an obstruction is present on the surface of the metal.

Place a small wad of cotton around the nickel coated nail and place in tap water. After a day or two, note that corrosion has started underneath the cotton.

The part of the nail that is uncovered has ready access to oxygen while the part under the cotton is deprived of oxygen and a corrosion cell is created. The part of the nail under the cotton becomes the anode and the rest of the nail the cathode. The metal part covered by the cotton ionizes and the electrons flow to the area surrounding the cotton.

Remove the cotton and observe your results.

CORROSION PROTECTION

There are a number of ways for preventing corrosion of iron and steel.

The metal can be coated to prevent moisture from reaching its surface. Zinc, tin, lead, nickel are used to coat steel. Most anti-corrosive compounds seal the surface of the metal from air and water by coating it or by combining with the metal.

A coating of oil and grease in machinery helps prevent corrosion of the moving parts by repelling water.

Even a coating of grease, if every part of the metal is covered will prevent corrosion.

Experiment 17. Cover one of your plain steel nails with a fat, such as vegetable shortening, rubbing it in well to be sure the surface is completely covered and place in water.

Examine it the next day. Does it remain uncorroded? If you have completely coated the nail and no water can reach its surface, it should not rust.

Experiment 18. Place one each of your copper coated, galvanized and nickel plated nails in separate containers of tap water. Allow to stand in the water overnight and then examine them. Are there

signs of corrosion in any of the nails?

Experiment 19. To protect iron or steel from corrosion one of the most common methods is to coat it with a film of a metal that is more active or less likely to corrode.

Galvanized iron is iron coated with zinc, a metal more active than iron, to protect it from corrosion. Note that your specimen did not rust. Allow to remain in the water several more days and then examine again. No corrosion appears.

Galvanized iron is used for roofing, garbage cans, wire fences and for many other products and structures consistently exposed to the atmosphere.

In a galvanized object, the zinc corrodes instead of the iron and protects the metal. This is another example of cathodic protection.

Experiment 20. Using a metal file or a wire cutter, break the surface of the zinc coating on the galvanized nail to expose the steel beneath. Place the nail in tap water. Does the nail begin to rust from that point? Or does the zinc coating continue to protect the steel?

Wait a few days to see if rusting will begin.

Once started, does the corrosion progress rapidly? Is it confined to the dam-

aged spot?

If the zinc coating should wear away in certain areas on the surface of a galvanized bucket or roof will the remaining zinc continue to protect the steel that has been exposed? Why?

Experiment 21. Iron and steel materials are often plated with metals lower in the activity scale such as tin, nickel and copper. But these metals will protect iron only if the coating is absolutely flawless without even the most minute holes that may escape the naked eye.

Such tiny holes, called holidays, form pinpoints of highly active corrosive action. Corrosion at such pinhole areas of exposure progress much more rapidly than on uncoated iron. Why? The smaller the hole, the more active the corrosion cell created.

Did your nickel coated and copper coated nails begin to rust from certain spots? If so, the coating was not perfect.

The uncoated area of a steel nail partially plated with a less active metal such

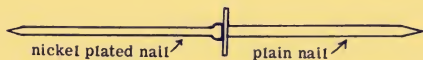


Fig. 3

as nickel corrodes much more rapidly than an uncoated nail.

Experiment 22. Take a nickel plated nail and a plain nail and place them end to end with the heads touching in a dish of water (Fig. 3).

Compare the extent and rapidity of corrosion of the uncoated nail in this experiment with the corrosion of the nail in Experiment 2, where the nail alone was placed in water.

Since iron is higher in the activity series than nickel it is more active and its corrosion is enhanced by the galvanic action taking place between these two dissimilar metals.

Thus, a coating that has worn away or that has been damaged increases the rate of corrosion of the metal it was meant to protect.

Experiment 23. Note that the enamel covered stove and refrigerator and other equipment in your home is a protective coating for the steel underneath. A simple test to show that the metal is made of iron is to see if the metal will attract a magnet.

If the enamel is chipped it will rust from that point and the corrosion unless checked could gradually work its way into the metal under the enamel coating doing

extensive damage.

Chromium is another popular coating for iron as you have observed in automobiles and a variety of instruments.

Some alloys, such as stainless steel, a chromium alloy steel, are especially designed for strength and corrosion resistance. All of you have observed how resistant this metal is to corrosion.

Tin cans are not really made of tin, but are constructed of steel coated with tin to protect the can against corrosion. In some cases the tin itself is again coated with enamel to maintain the color of the contents such as corn and peas.

Experiment 24. Take the top of an open tin can and leave it in a moist environment. Note how quickly corrosion takes place along the cut edge where the iron is exposed. Can you explain why corrosion spreads so fast in such cans?

Tin is less active than iron and therefore becomes the cathode in the electric cell formed by the two metals.

Experiment 25. Bury near each other a plain nail and a plain nail with $3\frac{1}{2}$ inches of magnesium ribbon attached in the soil of a potted plant or outdoors. Be careful to keep the nails separated so that they do not touch each other. After a day or two unearth them and examine the

results. Which nail is rusted?

Soil varies in different areas of the country. Therefore, the amount of corrosive action on iron pipes varies from place to place, occurring more readily in clayey soils than porous soils where moisture is not retained.

Experiment 26. Bury a copper coated nail with the remaining magnesium in contact with it. Does it protect the copper coated nail as well?

The mineral content of water varies from place to place. Therefore some waters are more corrosive than others.

Copper pipes are used in many areas because of its resistance to corrosion. However, in locations where the water is high in carbon dioxide, sulfate or chloride, it will go into solution very slowly, and although this dissolution of copper is not too serious to the pipe itself, water containing only a minute quantity of dissolved copper will cause pitting of aluminum or galvanized iron (see Experiment 10). Aluminum is especially susceptible particularly when chloride ions also are present in the water.

Experiment 27. Devise an experiment to demonstrate the effect of copper on aluminum.

Experiment 28. Brass is an alloy

of copper and zinc. Can you make up an experiment to show the corrosive action of brass?

Experiment 29. Think up other corrosion experiments.

There are many varieties of anti-corrosion products available to the consumer for use on tools, machinery or to protect car radiators.

The main purpose of all these products is to inhibit the formation of a corrosion cell. It may be done by making the electrolyte non-conducting or interfering with the passage of the electric current from the anode to the cathode.

There are many ways in which corrosion may occur when metal is exposed to environmental conditions of weather, ocean or soil. However, basically the process is one of electrochemical action as shown in experiments you have just performed.

Continuous study goes on in this field for its control, and many books have been written on the subject.

If you wish to read further on the subject, here are a few references:

Elementary chemistry books.

Corrosion and Corrosion Control, H. H. Uhlig, J. Wiley & Sons, Inc., New York, 1963.

Corrosion and the Maintenance Engineer, C. L. Wilson and J. A. Oates, Hart Publishing Co., Inc., New York, 1968.

Electrochemistry, Edmund C. Potter, Cleaver-Hume Press Ltd., London, 1957.

Appreciation is expressed to John R. Ambrose, National Bureau of Standards, Washington, D.C., for reviewing this booklet for technical content.

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